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Ice-Catalyzed Ionization of Hydrochloric Acid

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Abstract: Ionization of hydrochloric acid (HCl) on stratospheric ice particles is believed to be a key step in the depletion of stratospheric ozone. Ab initio calculations based on a model HCl−water cluster show that HCl ionization *on* ice surfaces is a barrierless process. Since this mechanism is rapid and produces chloride anions that are exposed to ambient stratospheric chlorine reservoir molecules, it is likely to be important for stratospheric chemistry. It complements a previously suggested mechanism where HCl forms part of the ice lattice before ionizing. The mechanism proposed here is also consistent with experimentally observed ionization of HCl on ice at low temperatures and under vacuum, where the HCl is not expected to be encapsulated in the ice lattice.

Introduction

Stratospheric ozone protects the earth from the harmful ultraviolet (UV) radiation in sunlight that, among other things, causes skin cancer.[1] Depletion of this ozone layer and the formation of ozone holes is linked to the presence of polar stratospheric clouds (PSCs).[2] These particles provide surfaces for catalyzing important chemical reactions such as

$$\mathrm{HCl} + \mathrm{ClONO_2} \rightarrow \mathrm{Cl_2} + \mathrm{HNO_3} \qquad (1)$$

and

$$\mathrm{HCl} + \mathrm{HOCl} \rightarrow \mathrm{Cl_2} + \mathrm{H_2O} \qquad (2)$$

Chlorine (Cl_2) produced in these reactions photodissociates to Cl atoms which react with and deplete ozone.[3]

Numerous experimental and theoretical studies (e.g., refs 4−19), which have aimed at identifying the mechanisms and rates of the above reactions, have often been based on pure water ice surfaces. Although the structure and composition of PSC particles has not been unequivocally identified, they are believed to consist primarily of water.[20−23] PSC particles that were observed in recent field measurements between 188 and 195 K were ternary solutions of H_2O, HNO_3, and H_2SO_4, with increasing relative water content at lower temperatures.[20] Below the ice frost point PSCs are expected to consist of water condensed on binary or ternary nucleation sites.[22] Thus pure water ice surfaces, as used in previous and the present studies, provide a good starting point for studies of heterogeneous stratospheric reactions.

There is substantial experimental evidence that HCl exists in its ionized form on ice surfaces under stratospheric conditions and on low-temperature ice surfaces under vacuum,[7−11] and that surface phase chloride ions (Cl^-) react with the chlorine reservoir molecules in reactions 1 and 2 to produce Cl_2. However, the mechanisms of HCl ionization and of reactions 1 and 2 are not well understood. For example, if $ClONO_2$ and HOCl are molecularly adsorbed on the ice surface, then the Cl^- ion must be on or near the top of the ice surface for reactions 1 and 2 to occur.

Hynes and co-workers performed molecular dynamics simulations to study HCl ionization on crystalline pure water ice surfaces.[12] They found that when an HCl molecule replaces a surface water molecule, so that the HCl forms part of the ice lattice, ionization is barrierless and thermodynamically favorable. This mechanism may be relevant under stratospheric conditions, since the adsorption and desorption rates of water at the surface are approximately $10-10^3$ monolayers per second,[24] and HCl can thus be trapped in the ice lattice. Recent molecular dynamics

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simulations[25] indicate that molecular HCl can penetrate into the ice lattice, which may also lead to encapsulation of this molecule in the lattice structure.

Ab initio calculations of HCl ionization *on* the ice surface (i.e., where the HCl is not part of the ice lattice) indicated that this reaction has a large 20−32 kJ mol^{-1} barrier and is not thermodynamically favorable.[13] These calculations included nine surface water molecules and, to maintain the crystalline ice geometry, the water oxygen atoms were fixed in their crystal lattice positions. The conclusions obtained from these ab initio calculations differ from those of an earlier molecular dynamics study of Robertson and Clary, which indicated that HCl ionization on an ice surface is energetically feasible.[14] In agreement with this molecular dynamics study, recent quantum mechanics/molecular mechanics (QM/MM) simulations indicated that HCl ionization on the ice surface may, in fact, be barrierless.[15] The discrepancy in these results with the ab initio calculations[14] was explained by the fact that ionization requires significant relaxation of the ice surface, especially of the hexagon where HCl ionization occurs. Constraining the oxygen atoms in their lattice positions during the QM/MM simulations, as was done in the ab initio calculations, prevents HCl ionization. A second requirement crucial for ionization is that the hexagon where the ionization occurs must have two dangling hydrogens. An HCl molecule impinging on a hexagon that has zero, one, or three dangling hydrogens hops from one hexagon to another until it lands in a hexagon with two dangling hydrogens, where it ionizes.[15] This is illustrated in Figure 1.

The validity of the dynamics observed in the QM/MM simulations depends, among other things, on the accuracy of the interatomic forces. The forces between the water molecules in the MM region were obtained from the TIP4P potential surface,[26] which has been used successfully to study ice surface dynamics under stratospheric temperatures.[27,28] The QM region consisted of the reacting HCl molecule and either 12 or 24 water molecules (which may be intimately involved with ionization). The forces between the QM atoms were obtained from electronic structure theory calculations at each trajectory step, which allows for the simulation of complex chemical reactions (which are often difficult to describe using simple analytic functions) as well as implicitly including instantaneous polarization effects (which is known to be important for water molecules in the condensed phase). Due to the expense of ab initio calculations, the PM3 semiempirical method[29] was used in the QM/MM study. The accuracy of the PM3 model for the HCl−ice system was tested by comparing energies and geometries of small HCl−water clusters with data obtained from ab initio calculations.[15,30] The PM3 parameters were fine-tuned until agreement between the semiempirical and ab initio data was obtained. The resulting semiempirical model was called PM3 with system specific parameters (PM3-SSP).

Although the PM3-SSP model provides an accurate description of the HCl−water structures used in the fitting procedure, there is no guarantee that it provides as good a description for other geometries relevant to the simulations, or to the larger HCl−ice system used in the study. This raises the question as to whether the observed HCl ionization on ice surfaces is, in fact, barrierless or whether it is an artifact of the PM3-SSP potential. To confirm (or refute) the QM/MM results, we have performed ab initio geometry optimizations[31] of HCl on ice.

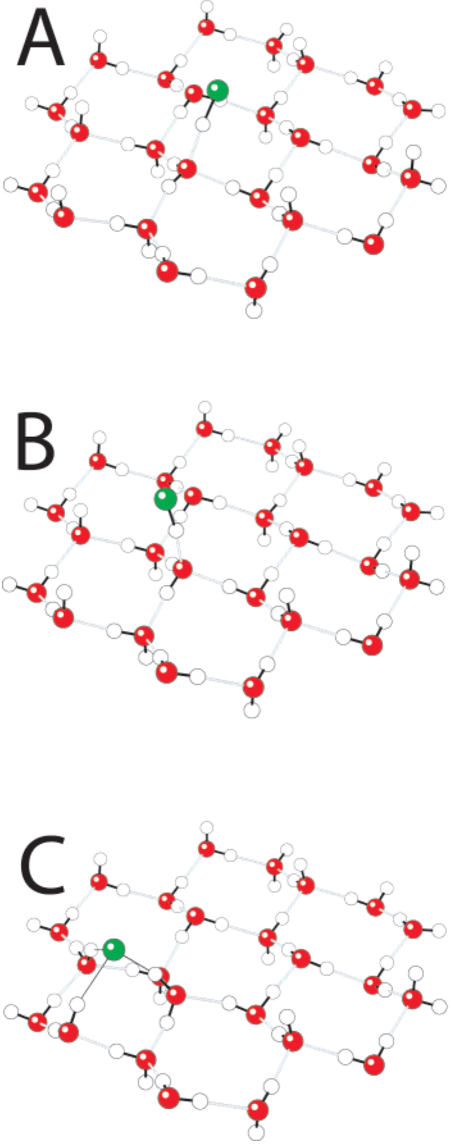

Figure 1. When an HCl molecule impinges on an ice hexagon that has 0, 1, or 3 dangling hydrogens (in panel a it has 0 dangling hydrogens) it hops (panel b) across the ice surface until it finds a hexagon with 2 dangling hydrogens (panel c). These hydrogens facilitate HCl ionization by solvating the Cl$^-$ anion. This figure is of a damped (0 K) QM/MM trajectory, where thermal distortions from the crystalline ice lattice are negligible. Similar hopping dynamics are observed at stratospherically relevant temperatures.[15] Only 30 of the 768 water molecules used in the simulations are shown in the figure.

Method

Previous calculations of HCl−water systems have shown that the MP2 method with a 6-31G(d) basis set yields qualitatively (and even semiquantitatively) accurate structures and energies for this system,[32] and that the MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels give quantitatively accurate results.[32−34] All three methods are too expensive to allow for a large ice surface to be included in the optimization, and thus a small section of the ice surface, consisting of 15 water molecules, is assumed to provide a reasonable model of the entire surface.[35] Since the QM/MM simulations showed that relaxation

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(30) This comparison was limited to clusters including 1−4 water molecules due to the computational expense of the ab initio methods.

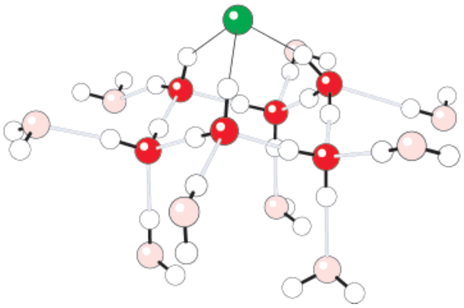

Figure 2. The minimum energy HCl−ice structure obtained at the MP2/6-31G(d) level. The central water molecules (red oxygen atoms) are unconstrained during the geometry optimization, whereas the neighboring water molecules (pink oxygen atoms) are constrained in their crystalline lattice positions.

of the ice surface is crucial for ionization (especially for the hexagon where the ionization occurs), the positions of the 6 inner water molecules were not constrained during the optimization (see Figure 2). The 9 neighboring water molecules were constrained in their crystal lattice sites to maintain the correct ice geometry. Two of the inner water molecules, which form part of the central hexagon, had dangling hydrogens, which is also required for ionization. The HCl was initially 8 Å above the ice surface in the optimization.[36]

Results and Discussion

Geometry optimization, performed at the MP2/6-31G(d) level,[37] leads directly to HCl ionization. Thus, as observed in the QM/MM simulations, HCl ionization on the ice surface is barrierless.[38,39] The optimized (minimum energy) structure is shown in Figure 2. The crystalline structure of the hexagon is distorted such that the H_3O^+ is shifted toward the center of the hexagon, and the dangling hydrogens point toward the Cl^- ion, thereby solvating and stabilizing the product anion. The H−Cl separation, which is 1.28 Å when the HCl is 115 Å above the ice surface, is 1.89 Å in the minimum energy structure, and the effective charge on the chlorine changes from −0.24 for an HCl−ice separation of 115 Å to −0.79 for the minimum energy structure.

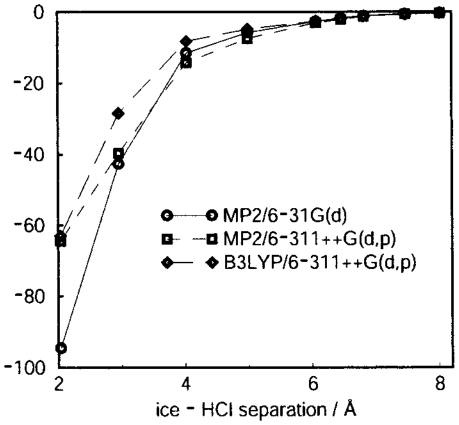

Figure 3. Energy of the HCl−ice system (shown in Figure 2) along the MP2/6-31G(d) optimization path. The distance between the ice surface and the chlorine atom is shown on the *x*-axis. The circles show the MP2/6-31G(d) energies, the squares show the MP2/6-311++G(d,p) energies (obtained for the corresponding MP2/6-31G(d) geometries), and the diamonds show the B3LYP/6-311++G(d,p) energies (also obtained for the MP2/6-31G(d) geometries). The curves are drawn to aid visualization. It is evident that HCl ionization on ice surfaces is barrierless.

To test the effect of increasing the basis set size and changing the ab initio method, 9 HCl−ice structures along the MP2/6-31G(d) optimization path were selected and their energies were recalculated at the MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels.[40] These energies are presented, together with the MP2/6-31G(d) energies, as a function of the HCl−ice separation in Figure 3. It is evident that there is no barrier to HCl ionization at any of the three levels of theory, and that the two higher levels give similar results.[41]

The ab initio calculations presented here show that HCl ionization on pure water ice surfaces is barrierless, as was seen in the QM/MM simulations. This exemplifies one of the ways in which the QM/MM method can be used, i.e., to identify probable reaction mechanisms using a lower level of electronic structure theory, before confirming them using high-level stationary point calculations and/or geometry optimizations. The knowledge gained from the simulations (in this case the importance of surface relaxation and number of dangling hydrogens) is used when planning computationally demanding ab initio calculations.

In the mechanism presented here the Cl^- product anion lies above the surface, and is not part of the lattice structure (see Figures 1 and 2). It would thus be exposed to ambient gases found in the stratosphere, such as $ClONO_2$ and HOCl. Experi-

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(35) The validity of this assumption was tested using the PM3-SSP model, where optimization of the HCl−ice system was performed using both the complete ice surface used in the QM/MM simulations and a segment of this surface that included the 15 water molecules nearest to the HCl. The similarity of the energy changes obtained for these two models supports the assumption that the 15 water molecules neighboring the HCl dominate the energy changes during the ionization, and thus provide a good model for the ice surface.

(36) The MP2/6-31G(d) energy for the HCl−ice system when the HCl is 8 Å above the surface is only 0.27 kJ mol^{-1} lower than when the HCl is 115 Å above the surface. For the MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) the energy differences are 0.34 and 0.28 kJ mol^{-1}, respectively.

(37) The MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels were computationally too expensive to be used in the optimization. The optimization at the MP2/6-31G(d) level took more than five CPU weeks on a 195 MHz R10000 SGI processor.

(38) The geometry optimization for HCl−ice separations between 8 and 5 Å was repeated using a maximum optimization step size of 0.027 Å to confirm that a barrier was not present.

(39) Changes in the zero point energy along the optimization path are not expected to lead to an effective barrier. The HCl−ice structure when the HCl−ice separation is 5 Å (see Figure 3) is very similar to the structure when the separation is 115 Å. For example, the HCl bond length is 1.28 Å for both structures. This indicates that changes in the interatomic forces between these structures are very small, and hence their zero point energies are expected to be similar.

(40) These are MP2/6-311++G(d,p)//MP2/6-31G(d) and B3LYP/6-311++G(d,p)//MP2/6-31G(d) calculations.

(41) The similarity of the MP2/6-31G(d) and MP2/6-311++G(d,p) energies for HCl−ice separations between 3 and 8 Å indicates that basis set superposition errors are not likely to induce a barrier. The difference in these energies for the optimized geometry indicates that basis set superposition errors may be large for this structure.

mental and theoretical studies of $ClONO_2$−HCl−ice and HOCl−HCl−ice systems, where the HCl is initially in its ionized form and is exposed to $ClONO_2$/HOCl, indicate that the formation of Cl_2 is barrierless or involves a negligible barrier.[8,9,42,43] Thus, the mechanism of HCl ionization presented here is likely to be important in stratospheric chemistry, and complements the mechanism proposed by Hynes and co-workers.[12] The dynamic nature of the ice surface under stratospheric conditions may lead to the encapsulation of the Cl^- ion in the ice lattice before it reacts with an ambient gas molecule and, similarly to the situation found in the Hynes mechanism, it must diffuse to the surface before reaction with ambient molecules can occur. For low-temperature ice surfaces, and for surfaces under vacuum,[10,11] where evaporation and condensation of surface molecules is very slow, the ionization mechanism presented here may dominate and the surface lifetime of the Cl^- ion is expected to be long.

It has been suggested that ice particles at stratospheric temperatures have liquidlike surfaces.[44−46] The mechanism discussed here does not require the presence of a liquidlike surface, although significant relaxation of the surface layer is required. However, QM/MM simulations at 180 K revealed the possibility for flipping of surface water molecules,[15] which is associated with liquidlike properties at the surface.[45] Flipping of these molecules changes the number of dangling hydrogens in the surface hexagons, and hence affects the ionization process.

Conclusion

The MP2/6-31G(d), MP2/6-311++G(d,p), and B3LYP/6-311++G(d,p) calculations presented here show that HCl ionization on pure water ice surfaces is barrierless. The Cl^- product anion, which lies above the surface and is not part of the lattice structure, would be exposed to ambient gases found in the stratosphere. This ionization process is thus likely to be relevant to stratospheric chemistry and ozone depletion.

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